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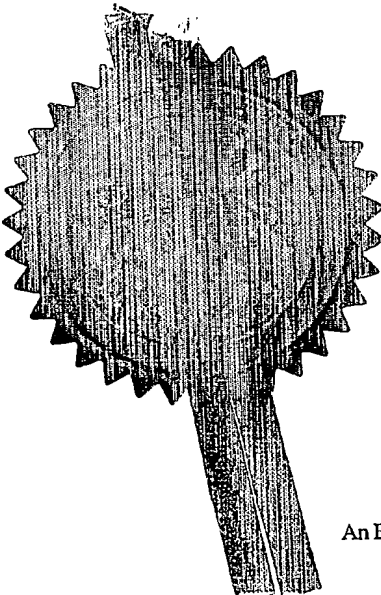
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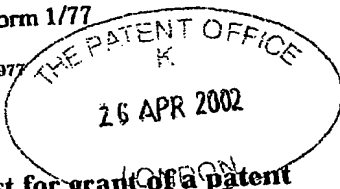


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METHOD

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METHOD

The present invention relates to a method of improving the thermal oxidative stability of a distillate fuel.

Current jet engine fuels have to meet an extensive list of criteria, including corrosion, material compatibility, freeze point, heat of combustion, conductivity and stability, including storage stability and thermal oxidation stability.

In particular, thermal oxidation stability relates to the stability of the distillate jet fuel at elevated temperatures, such as in the aircraft fuel system and engine. Jet fuels need to meet certain thermal stability specifications to comply with international operational safety requirements.

The current thermal stability specification test method for the most widely used commercial and military aviation jet turbine fuels, ASTM D3241, is based on the Jet Fuel Thermal Oxidation Tester (JFTOT). The JFTOT method is based on measurement of deposition occurring on heated surfaces, and employs a standard electrically heated 6061 aluminum tube, typically at 260°C, over the surface of which pre-aerated fuel flows.

Failures in the JFTOT may result from specific deposit coloration on a heated aluminum tube surface or, less frequently, from excessive pressure resulting from the formation of filterable particulates.

For a general review of the area of thermal stability see Hazlett, RN. "Thermal Oxidation Stability of Aviation Turbine Fuels", American Society for Testing and Materials, 1991.

Numerous chemical factors have been linked with the problems of thermal oxidative stability. Although forming only a minor proportion of the fuel, the majority of the deposits formed have been attributed to reactions of relatively minor components present. For example, auto-oxidation has been proposed to be a significant process for deposit formation, and compounds containing oxygen, sulphur, nitrogen and metals have all been linked to the extent of deposit formation.

However, thermal oxidative stability has been shown to vary strongly between different fuels. Although individual components have been identified as contributing to problems of stability in certain fuels in certain situations the previous results have often been contradictory or have been performed under experimental conditions or at temperatures inconsistent with the standard JFTOT test.

It has now been surprisingly found that the majority of deposits formed in the JFTOT test are derived from specific components in the fuel, in the presence of certain metals.

Thus, according to a first aspect of the present invention there is provided a method for improving the thermal stability of a distillate fuel which comprises reducing the active concentration of N-H containing heterocyclic aromatic compounds present in the fuel, and wherein said fuel also contains an active concentration of metal compounds or will be exposed to active metal compounds in storage or in use.

According to a second aspect of the present invention there is provided a method for improving the thermal stability of a distillate fuel which comprises reducing the active concentration of metal compounds in the fuel, wherein the fuel also contains N-H containing heterocyclic aromatic compounds.

According to a third aspect of the present invention there is provided a method for improving the thermal stability of a distillate fuel which comprises reducing the active concentrations of both N-H containing heterocyclic aromatic compounds and metal compounds present in the fuel.

By performing JFTOT tests on model fuels, and analysing the deposits formed using ellipsometry, it has been found that the deposit formation is strongly influenced by the co-presence of both certain metal compounds and certain N-H containing heterocyclic aromatic compounds. In the absence of either component the thermal stability of the fuel is significantly increased.

Relative to these components, certain other compounds, including other nitrogen compounds, sulphur compounds and oxygen compounds have been found to have a relatively smaller effect on deposit formation, regardless of the presence or absence of the metal compounds.

5 Hence, for a fuel containing both the certain metal compounds and deleterious N-H containing heterocyclic aromatic compounds, the thermal stability of the fuel can be significantly improved by either reducing the active concentration of the metal compounds, or alternatively by reducing the active concentration of the N-H containing heterocyclic aromatic compounds, or alternatively by reducing both components.

10 The deleterious N-H containing heterocyclic aromatic compounds are preferably those in which the electrons of the nitrogen atom of the N-H group can interact with the aromatic system. Examples of such compounds include pyrrole, indole, pyrazole, carbazole, substituted pyrroles, indoles, pyrazoles and carbazoles, and related compounds. Such nitrogen atoms, as part of the aromatic system, have a significantly
15 reduced basicity compared to conventional amines. Without wishing to be bound by theory it is believed that this property makes the ring more reactive to coupling and polymerisation type reactions, and hence makes these compounds susceptible to reactions leading to deposit formation.

 Certain metals or metal compounds have now been found to contribute to the
20 deposition process. Again without wishing to be bound by theory it is also believed that these metals and metal compounds may catalyse at least a part of the deposition process.

 Metals typically present in a distillate fuel may include copper, iron, lead and zinc. Typically these are present at low levels, such as in the parts per billion range (ppb). The active metal compounds which it may be desirable to remove or reduce
25 preferably comprise transition metals and most preferably comprise copper and/or iron compounds present in the fuel. Most preferably the active metal compounds which it may be desirable to remove or reduce comprise copper compounds.

 However, even where such metals are not present in the fuel initially or the active concentration of such metals is otherwise reduced, the fuel may be exposed to
30 active metals in storage and in use. For example, the US Navy has encountered problems with copper contamination of JP-5 fuels on aircraft carriers. As a further example, where the fuel is exposed to steel, such as stainless steel, the fuel may be

exposed to any of the transition metals present in the steel and/or these metals may potentially leach in to the fuel. Hence in cases where the fuel is likely to be exposed to further active metals any method for the reduction of active metal components at source may not have a significant effect after storage or in use. Methods that reduce the amount of active metals, such as copper, to which the fuel is exposed or otherwise prevent the formation of active metal species are hence preferred.

In general, problems of deposit formation are particularly an issue when the fuel is at temperature, such as just prior to combustion, for example, in nozzles. However, where fuel is stored for long periods of time, such as on aircraft carriers, then although slower the degradation of the fuel over time can also be an issue. In addition, the fuel can also be circulated as a coolant prior to use which may increase the extent of degradation before use.

As described above the methods of the present invention comprise reducing the active concentration of deleterious N-H containing heterocyclic aromatic compounds and/or the active concentration of metal compounds present in the fuel.

The active concentration of the deleterious N-H containing heterocyclic aromatic compounds may be reduced by any known method. In one embodiment this may include physical removal of at least a portion of said compounds from the fuel, for example by treatment with a suitable adsorbent material. Preferably the suitable adsorbent material is rendered specifically active towards said compounds. Specific adsorption, as distinct from general removal of polar species, will prolong the lifetime of the adsorption unit by increasing the time for saturation to occur. Specific adsorption may also increase the ease by which regeneration can be achieved, owing to the specific nature of the adsorbed species. Specific adsorption may be obtained by surface modification of common adsorbents to tailor the adsorbent for the specific chemical species, as is known for a range of different applications. For example, specific adsorption techniques are well known from developments in chromatographic stationary phase technology and could be readily applied to removal of species according to the present invention. For example, the relatively low basicity of the deleterious N-H containing heterocyclic aromatic compounds, such as pyrroles, the active concentration of which are to be reduced in the present invention distinguish them from the more basic compounds also present in the fuel that have found to be less important in the deposit forming process.

Examples of suitable adsorbents include surface-modified clays, aluminas, silicas and zeolites.

In addition, as distinct to adsorbents, specific absorbents derived from size- or shape-selective materials may be used to reduce the active concentration of the deleterious N-H containing heterocyclic aromatic compounds.

Alternatively, or additionally, the reduction of the active concentration of the deleterious N-H containing heterocyclic aromatic compounds may be achieved by reacting the compounds to form species that are inactive or less active in the deposition reaction, for example by complexing the compound (including its participation as a "guest" in a molecular "host-guest" relationship), by addition of a protecting group to the N-H functionality, or by reduction of the reactivity of the compound by substitution of a substituent that makes the aromatic heterocycle less susceptible to deposit forming reactions.

The active concentration of the metal compounds present in the fuel may also be reduced by any known method. Suitable methods may or may not be molecularly specific in their action. In one embodiment this may include physical removal of at least a portion of said compounds from the fuel, for example by treatment such as ion exchange or by filtration through a suitable adsorbent, such as clay filtration.

Alternatively, or additionally, the reduction of the active concentration of metal compounds may be achieved by reacting the compounds to form insoluble species that may be removed from the fuel or by reacting the metal compounds to form species that are inactive or less active for the deposition reaction, for example by complexing the metal compound or by adding a metal deactivator (MDA) such as a chelating agent, for example disalicylidene-1,2-propandiamine. In one embodiment solid-supported metal chelators can be used whereby selective adsorption of metal species can occur. When used such complexing agents or metal deactivators should be compatible with the intended use of the fuel.

In a further embodiment both deleterious N-H containing heterocyclic aromatic compounds and active metal complexes may be selectively adsorbed by one supported adsorbent system comprising two specific adsorption sites. Where it is desired to reduce the active concentrations of both species this allows effectively simultaneous reduction.

Experimental Section

n-Dodecane (ex Aldrich) was used as the model hydrocarbon phase for the JFTOT studies. Samples of a jet fuel (Jet A-1, ex Coryton Refinery) with a breakpoint of 270°C were also used in several of the tests.

- 5 The following compounds were used as dopants in the typical ranges expected for such compounds in real fuels: pyrrole, 2,5-dimethylpyrrole, indole, 2-methylindole, 3-methylindole, 2-methylindoline, 2,4,6-trimethylpyridine, 3-methylquinoline, thianaphthene, benzofuran and indene.

Methods

- 10 JFTOT tests were conducted, unless stated otherwise under standard ASTM D3241 conditions, although temperature was varied in some tests. Standard 6061 aluminum and 316 stainless steel tubes were purchased from the manufacturer, Alcor. Deposition levels were quantified using an ellipsometric technique as described in C Baker, P David, S E Taylor and A J Woodward, *Proceedings of the 5th International*
15 *Conference on Stability and Handling of Liquid Fuels*, Rotterdam, 433-447 (1995) which is herein incorporated by reference. Deposit thickness measurements were made over the tube surface at regular intervals using a Philips "Fuel Qualifier" instrument, and the deposit volumes determined by integrating the thickness results. This approach was applied to both types of tube, after inputting the pre-determined baseline parameters for
20 aluminum and stainless steel.

Deposition on Aluminum JFTOT Tubes and Identification of Deleterious Species

- 2-Methylindole, thianaphthene (benzothiophene), benzofuran and indene, which are characteristic of some of the polar and olefinic components of distillate (including jet) fuels, were dosed at concentrations up to 250 mg l⁻¹ to a sample batch of Jet A-1
25 fuel (J1), and the JFTOT test run at temperatures up to 280°C. The results are shown in Figure 1.

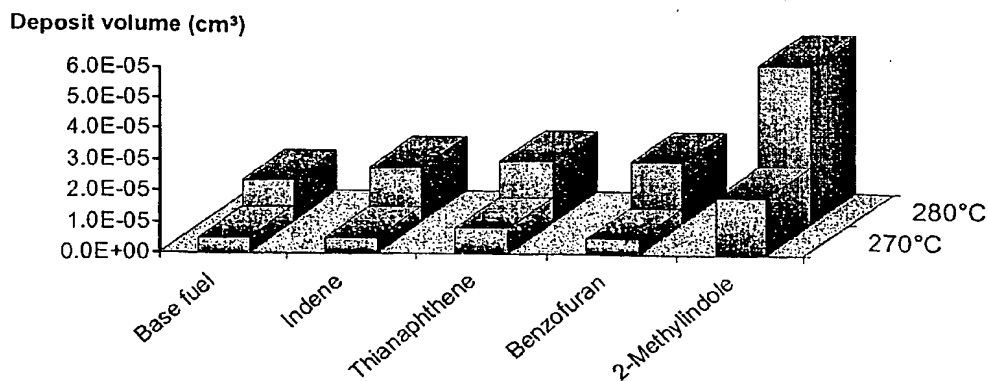


Figure 1. JFTOT screening of different compounds in Jet A-1 (J1) at 270 and 280°C on aluminum tubes.

It is evident from the results of this initial screening that the most significant deposition occurs in the presence of 2-methylindole at the test temperatures of 270 and 280°C.

Additional screening was carried out using dodecane dosed with the same compounds at concentrations up to 500 mg l⁻¹ and temperatures up to 340°C. In this case there was little evidence of deposit formation for any of the compounds tested. Figure 2 contains data for 2-methylindole, which exhibited the highest deposit-forming tendency when tested in J1.

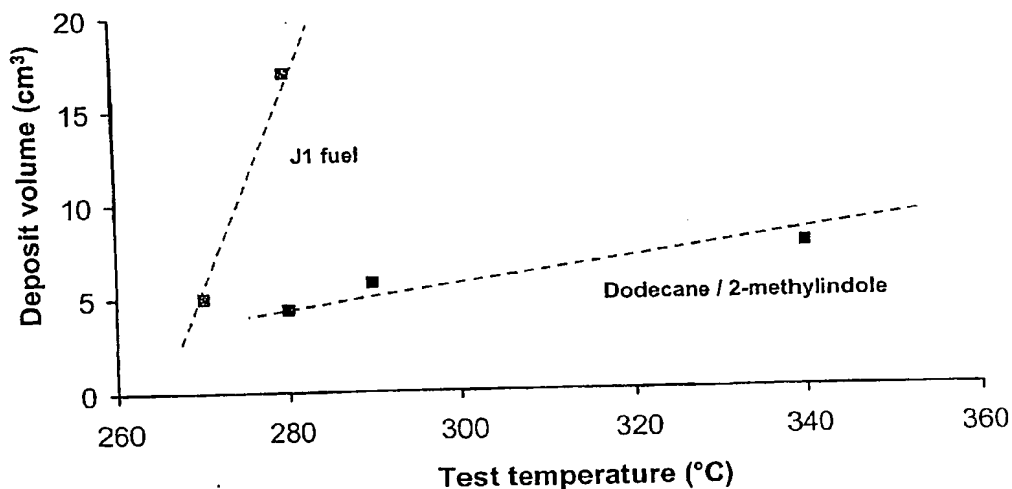


Figure 2. Comparison between deposition tendencies for J1 jet fuel and dodecane containing 250 mg l^{-1} 2-methylindole as a function of JFTOT test temperature.

Copper (II) naphthenate was then added at varying concentrations to the dodecane in the presence of 250 mg l^{-1} 2-methylindole, and the JFTOT test performed at 260°C . The results are shown in Figure 3.

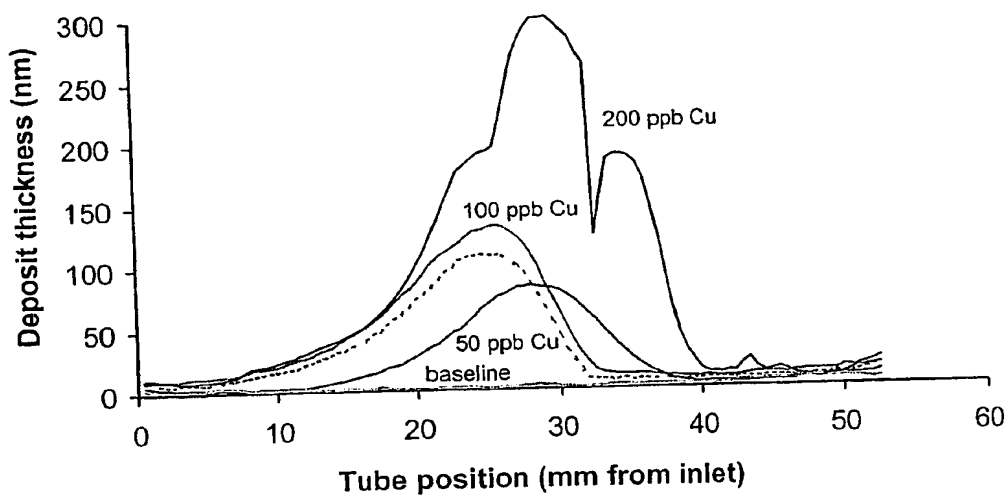


Figure 3. JFTOT tube profiles showing the effect of different copper(II) concentrations in dodecane on deposit formation in the presence of 250 mg l^{-1} 2-methylindole at 260°C .

The deposits in the presence of copper bore a strong resemblance to those generated from J1.

Thianaphthene, benzofuran and indene were also tested in an identical manner. However these substrates all showed low deposit volumes with no significant change in the deposition tendencies for these substrates in the presence of copper, compared with its absence. Figure 4 shows this for dodecane containing 100 ppb copper(II) and 250 mg l⁻¹ of thianaphthene at two temperatures.

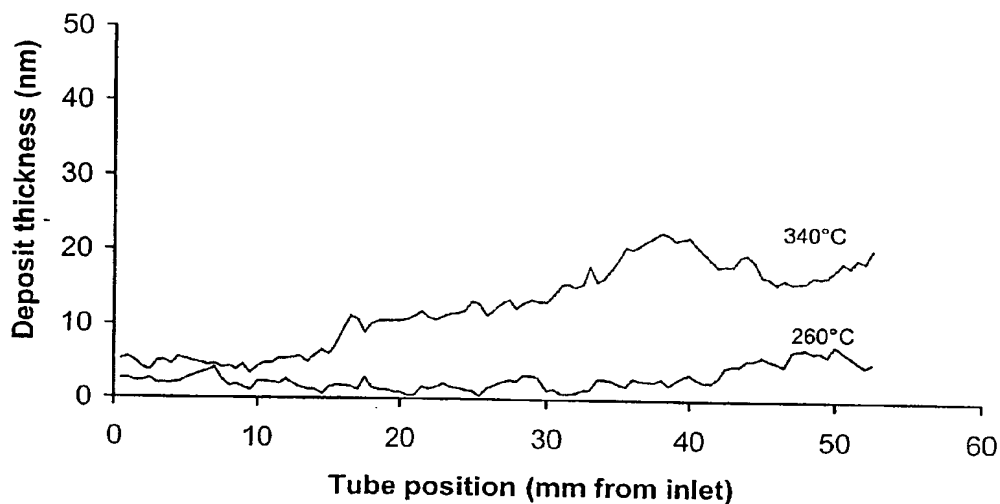


Figure 4. Aluminum JFTOT tube profiles showing the deposition occurring in dodecane containing 100 ppb Cu^{II} and 250 mg l⁻¹ thianaphthene at 260 and 340°C.

Further nitrogen-containing substrates (derivatives of quinoline, pyrrole and pyridine) were then tested in the same manner.

Figure 5 shows the effect of different concentrations of collidine (2,4,6-trimethylpyridine) and copper(II) on deposit formation from dodecane on aluminum at 260°C. The deposit formation was seen to be relatively low. The same effect was found for 3-methylquinoline. This behaviour was also found to be consistent with its behavior in J1 fuel.

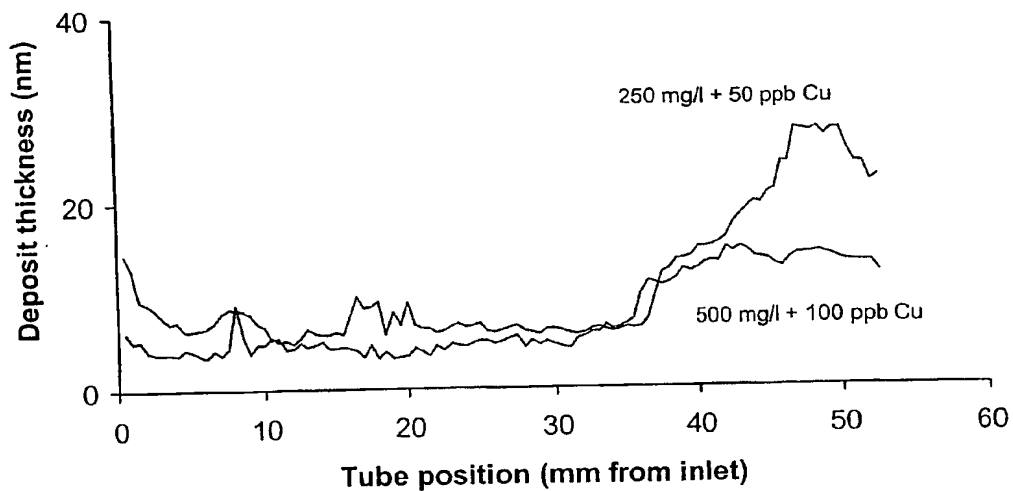


Figure 5. Aluminum JFTOT tube profiles showing the deposition occurring in dodecane containing different concentrations (indicated) of collidine and copper(II) at 260°C.

5 Pyrrole and 2,5-dimethylpyrrole were also tested. The results are shown in figure
6.

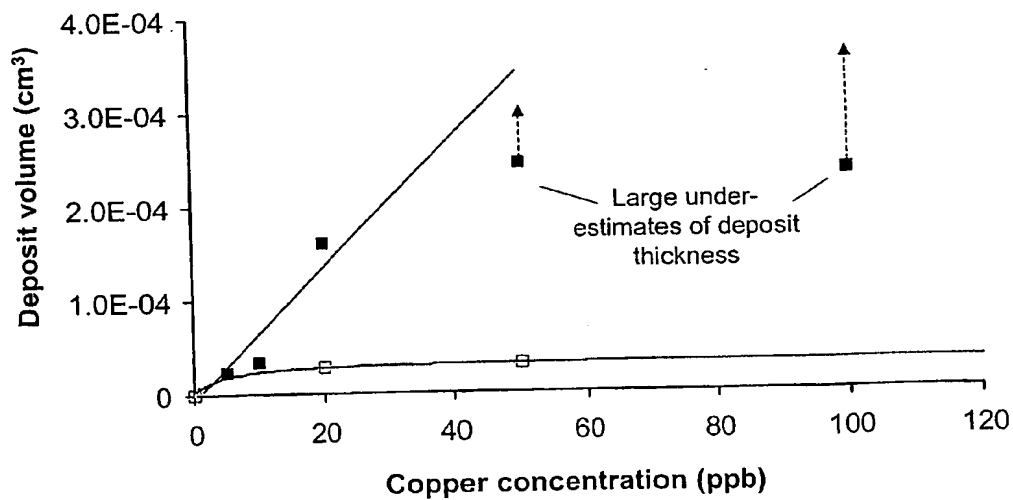


Figure 6. Dependence of JFTOT deposit volume on copper(II) concentration in the presence of pyrrole (open symbols) and 2,5-dimethylpyrrole (closed symbols) (aluminum tubes at 260°C).

Both pyrrole and 2,5-dimethylpyrrole produced significant levels of deposits, but it is evident that 2,5-dimethylpyrrole produced a greater level of deposits than pyrrole itself. As the data in Figure 6 shows, the deposits from the dimethyl- derivative become too thick for the ellipsometric technique to measure reliably.

- 5 Figure 7 shows the effect of addition of a metal deactivator (disalicylidene-1,2-propandiamine), in the case of the 2-methylindole system.

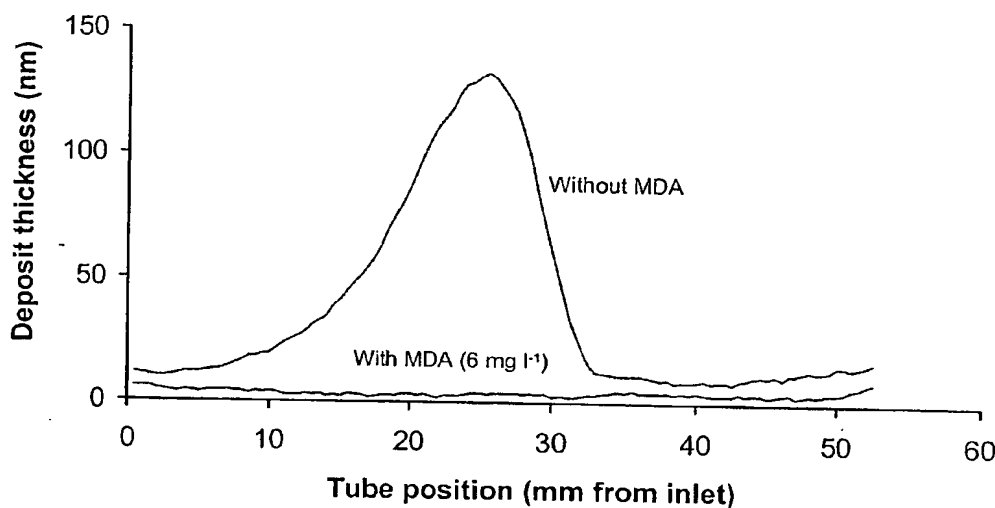


Figure 7. Effect of MDA (6 mg l⁻¹) on deposition produced from dodecane in the 2-methylindole (250 mg l⁻¹) / 100 ppb copper(II) system (aluminum tubes).

10 Deposition on Stainless Steel JFTOT Tubes

The following experiments were performed using stainless steel JFTOT tubes.

Figure 8 contains deposit profiles for JFTOT tests carried out on 2-methylindole (250 mg l⁻¹) in the presence different copper(II) concentrations. The presence of copper has a much less dramatic effect on stainless steel than found for aluminum tubes in

- 15 Figure 3, and deposits are seen even in the absence of added copper for 2-methylindole. The total deposit levels with 100ppb copper in dodecane containing 2-methylindole (250 mg l⁻¹) are similar on both aluminium tubes and stainless steel tubes under these conditions.

Deposits from thianaphthene in the absence of added copper however were still

- 20 low and comparable to the deposits seen on aluminium tubes.

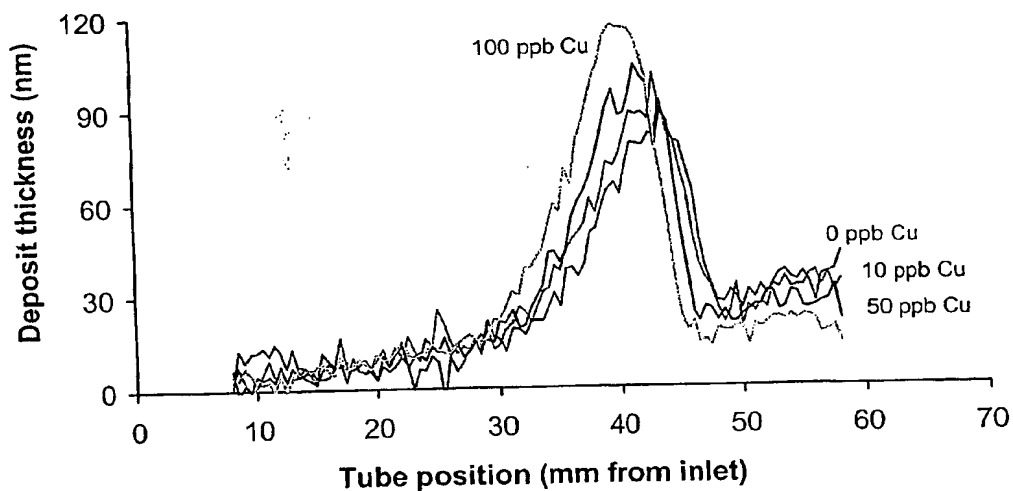


Figure 8. Stainless steel JFTOT tube deposit profiles showing the deposition occurring in dodecane containing 2-methylindole (250 mg l^{-1}) and different copper(II) concentrations at 260°C .

- 5 Figure 9 shows the effect of addition of a metal deactivator (disalicylidene-1,2-propandiamine), in the case of the 2-methylindole system on stainless steel. Again the use of a metal deactivator reduces the formation of deposits.

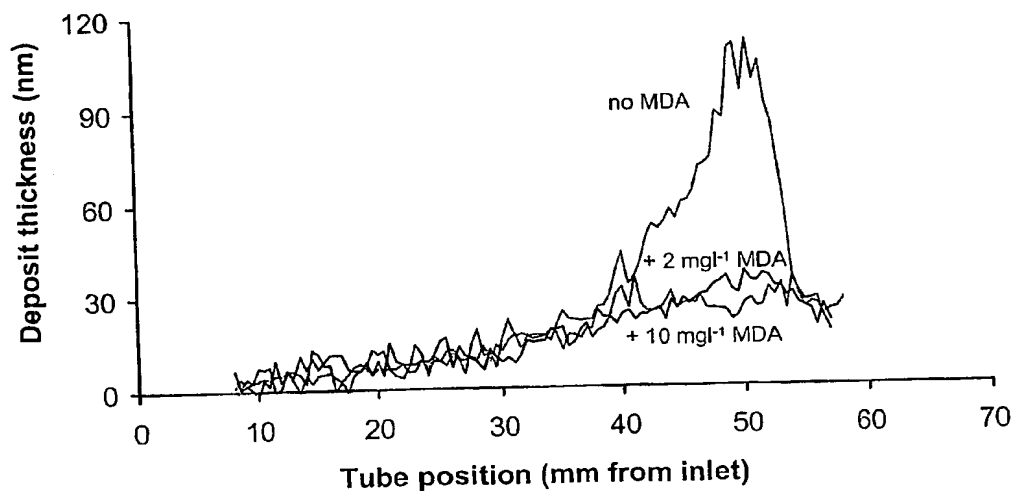


Figure 9. Effect of MDA on deposition produced from dodecane in the 2-methylindole (250 mg l^{-1}) / 100 ppb copper(II) system (stainless steel tubes).

Claims

1. A method for improving the thermal stability of a distillate fuel which comprises reducing the active concentration of N-H containing heterocyclic aromatic compounds present in the fuel, and wherein said fuel also contains an active concentration of metal compounds or will be exposed to active metal compounds in storage or in use.
- 5 2. A method for improving the thermal stability of a distillate fuel which comprises reducing the active concentration of metal compounds in the fuel, wherein the fuel also contains N-H containing heterocyclic aromatic compounds.
3. A method according to claim 1 or claim 2 which comprises reducing the active concentrations of both N-H containing heterocyclic aromatic compounds and metal
10 compounds present in the fuel.

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